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(21) International Application Number: PCT/US89/01980 (22) International Filing Date: 9 May 1989 (09.05.89) (30) Priority data: 225,116 27 July 1988 (27.07.88) US (71) Applicant: ASHLAND OIL, INC. [US/US]; P.O. Box 391, BL5, Ashland, KY 41114 (US). (72) Inventors: DOTSON, Daniel, J. ; P.O. Box 813, Huntington, WV 25712 (US). HAYNER, Roger, E. ; 1403 Christopher Court, Flatwoods, KY 41139 (US). (74) Agents: WILLSON, Richard, C., Jr. et al.; P.O. Box 391, BL5, Ashland, KY 41114 (US).		(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: REMOVABLE WATERBORNE TEMPORARY COATING (57) Abstract A waterborne temporary protective coating for the protection of vehicles during transit from manufacturer to automotive dealer. Combinations comprising acrylic emulsions, waxes, solvents, corrosion inhibitors, defoamers, amines, and surfactants provide temporary protection to painted and non-painted substrates and are easily removable without kerosene or steam. Also, being waterborne and removable with alkaline cleaners, they are non-detrimental to the environment.		

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REMOVABLE WATERBORNE TEMPORARY COATING

CROSS REFERENCES TO RELATED APPLICATIONS

USSN 124,655 (Attorney Docket 6255AUS) filed November 24, 1987 relates to the general field of the invention.

BACKGROUND1. Field of the Invention

The present invention relates to the field of corrosion resistant coatings, more particularly water based coatings for temporary protection of painted surfaces and easy removability. A major application is the protection of painted surfaces of automobiles during transit from manufacturer to distributor, including international transportation. Such compositions are sometimes called "transit waxes".

2. Prior Art

Various water-based compositions taught in the prior art, e.g. U.S. 4,659,380, U.S. 4,444,802, U.S. 4,444,803 all to Winters and Savell produce coatings for the protection of metal from corrosion.

Other waterborne coatings, e.g. U.S. 4,315,957 to Hereth et al. (Hoechst), utilize wax in waterborne formulations for protective coatings.

Some prior formulations are intended specifically for automobile permanent coatings, e.g. Japanese patent applications 62132-569-A and 62132-568-A (Kansai Paint KK) both of which use radiation to cure compositions containing radical polymerisable unsaturated compounds, such as epoxy resins and waxes.

-2-

Aqueous wax dispersions for preserving metal and lacquer are taught by West German patent DE 3512564 A1, 16 October 1986 to Ziegler et al. BASF AG).

All of the above coatings are basically permanent coatings and do not fill the object of the present invention to provide a temporary coating for protecting surface of automobiles, etc. temporarily, during transit.

Temporary coatings are taught by Kawabata (Nippon Oil) U.S. 4,442,140 which teaches compositions containing oxygen-containing wax, emulsifying agent, talc or other silica, other solid pigment or filler. U.S. 4,442,140 compositions tend to flake off and stain as noted at its column 1, line 33-37.

U.S. 4,594,109 also to Kawabata (Nippon Oil) comprising oxygen-containing wax, polybutane, silicone oil, various fillers and an emulsifier. The use of silicone oil precludes any over-spraying, e.g. to cure minor defects or pitting damage during transit.

Therefore, neither of these formulations is well-suited to protection of automotive coatings, even though these compositions are designed to be removable.

Even with those formulations which are water-based and which are designed for reasonably efficient removal of the temporary coating, many require removal with hot steam and solvents, e.g. kerosene, others particularly those employing wax will cause difficulty in removal and possible staining of the undercoating. Others, e.g. water-based amine-containing compositions, can cause softening of the permanent coating which they are intended to protect. Most waxy formulations provide only

-3-

a hazy or opalescent finish, detracting substantially from the appearance of the automobile or other coated object which they are protecting and may obscure vision through the windshield during drive-on, drive-off operations. As mentioned above, some formulations have prevented over-coating, particularly those formulations which contain silicone. Many wax-containing (water-or solvent based) formulations present a soft waxy film which retains dirt, creating unsightly appearance after long transportation. Solvent based formulations generally present health hazards in the work place where they are applied and removed as also do coatings which require steam and solvent combinations for their removal.

SUMMARY

1. General Statement of the Invention:

According to the present invention, it has been discovered that waterborne, optionally clear, protective coating for protection of new vehicles in transit and the like which is easily removable without harm to the underlying permanent coating can be formulated from: acrylic emulsions, preferably alkali soluble acrylic emulsions, amines, particularly aqueous ammonia and amines such as morpholine, triethylamine/triethanolamine (TEA), dimethylethanolamine (DMEA), diethylaminoethanol (DEAE), 2-amino, 2-methyl -1- propanol (AMP 95).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a bar graph of comparative Weatherometer test results of the invention versus several comparative conventional formulations as set forth in the Examples.

-4-

Figure 2 is a schematic of an article of manufacture comprising a painted metal substrate coated with a composition of the invention.

DESCRIPTIONS OF THE PREFERRED EMBODIMENTS

STARTING MATERIALS

Acrylic Emulsions

Preferably the compositions of the present invention will include acrylic emulsions, and more preferably those which are alkali soluble. A preferred acrylic emulsion having film forming characteristics at ambient temperatures and a glass transition (T_g) of 5-40°C. Non-volatile content should be in the range of about 30-50% by weight. Acid value of the acrylic should be in the range of about 75-150 which allows for alkali solubility.

Preferred commercial acrylic emulsions would include Neocryl BT520 from Polyvinyl Chemical and Carboset 514H or XPD-1214 from B.F. Goodrich.

The amount of acrylic emulsion to be utilized for the present invention is not narrowly critical. For most formulations, the acrylic resin content will be from about 0.5 to 90, more preferably from about 10 to about 60, and most preferably from about 20 to about 60% by weight.

All percents given herein are percents by weight based on the weight of the total formulation unless otherwise expressly stated. These percents assume average concentration and, of course, can be greater

-5-

reduced by over-dilution with water and/or co-solvents without departing from the spirit of the invention.

Amine

The term "amine" as used herein, includes aqua ammonia. Aqua ammonia (preferably 28° Be) is the most preferred "amine" for purposes of the present invention. Other amines usable include morpholine, triethanolamine, dimethylethanolamine (DMEA), diethylaminoethanol (DEAE), preferably supplied commercially as "AMP-95", or others commercially available and used by those skilled in the art.

The amine will be present preferably in about 0.1-20 parts by weight, more preferably 1.0-10, and most preferably about 1-5 parts by weight. The most preferred amine is about 1-5 parts by weight of aqueous ammonia (28° Be).

Cosolvents

Cosolvents are desirable, though not absolutely necessary, because they assist in rapid drying. Preferred cosolvents are alcohols, e.g. ethanol, Isopropanol or isobutanol; glycol ethers e.g. butyl cellosolve, cellosolve, methyl cellosolve, dipropylene glycol methyl ether (DPM), propylene glycol methyl ether (PM), and various others as may provide desired characteristics in blending and application for the particular formulation of interest.

Cosolvents will preferably be present in about 0-30 parts, more preferably 1-20 parts, and most preferably 1-10 parts.

-6-

Corrosion Inhibitors

The preferred corrosion inhibitors for the purposes of the invention are the most preferred metal passivator commonly known as Cobratec^R TT85 available from PMC Specialities, Cincinnati, Ohio, which is a sodium salt of tolytriazole. Other effective corrosion inhibitors are ammonium salts of dichromate and molybdate and the Corbratec benzotriazoles. SACI 445W emulsion from Witco Chemical and other calcium sulfonate emulsions can be used. Ammonium benzoates and sodium nitrites can also be employed in the formulations in the present invention. It has been found that experimental emulsion 31327X1 from Michelman, Inc., Cincinnati, Ohio, has a particular advantage in the present invention because it has been discovered to not only have both a corrosion inhibition, but also a stabilizing effect when used in the formulations of the present invention.

Corrosion inhibitors will generally be present in about 0.1-15, more preferably 0.1-10, and most preferably 0.5-5 parts by weight based on the weight of the formulation.

Surfactants

Preferred surfactants include non-ionic surfactants, e.g. Triton X-100, a 100% active octyl phenoxy polyethoxy ethanol having a HLB value of 13.5 and available from Rohm & Haas. Other non-ionic surfactants, e.g. Igepal, available from GAF may be used. Anionic and cationic surfactants may be used in specialized circumstances, but are generally not preferred because they have a tendency to attack the underlying paint film which is to be protected and because they may form unstable emulsions due to their

-7-

incompatibility with other ingredients. Triton X-100 is particularly preferred because it has a two-fold advantage. Triton X-100 imparts excellent surface wetting of the mixture, and also renders the cured film more sensitive to removal by hot water, providing additional ease in removability.

Surfactants will generally be present in amounts of about 0.1-10, more preferably 0.2-5, and most preferably 0.5-2.0 parts by weight based on the total weight of the formulation.

UV Additives

Though not required for the formulations of the present invention, their economics and solubility considerations will permit, various UV absorbers, hindered amine light stabilizers and anti-oxidants may be incorporated to lengthen or improve the desired protection provided to the underlying coating by the temporary films of the present invention. UV absorbers and HALS function to keep the acrylic resin from cross-linking from outdoor heat and UV exposure, and thereby permit longer periods of protection and provide films which remain easy to remove.

When used in the present invention, UV additives will generally be present in amounts of 0.05-5%, more preferably 0.1-2%, most preferably 0.15 to about 1% by weight, but these amounts are not narrowly critical.

Defoamers

In most of the formulations of the present invention, defoamers are valuable additives and any of the common defoamers currently used with water-based

-8-

acrylic formulations are acceptable. Particularly preferred is BYK 020 available from BYK-Chemie and SWS211 available from SWS Silicones Corp. in Adrin, Michigan.

Defoamers will generally be used in very small amounts ranging from a trace to 5.0, more preferably 0.01 to about 2, and most preferably 0.02-0.5 parts by weight based on the weight of the formulation.

Other Additives

Various corrosion inhibitors, wax emulsions, and additives commonly known to those skilled in the coatings art may be added to tailor specific properties desired in cured films according to the invention.

Techniques in Mixing

Apparatus: The apparatus for the present invention will be that conventionally utilized in the preparation of coatings compositions, e.g. kettles and mixing tanks having flow metering or measuring devices and agitation means, e.g. pumps mounted on side-arms connecting with the main vessel, internal stirrers, contra-rotating shearing devices and any of the other available devices which are well known to the art.

Temperature: The entire formulation of the present compositions can be accomplished at or near room temperature without need for expensive heated vessels, temperature control, etc. No substantial exotherm is involved during formulation of the compositions of the invention in most cases. The temperature during mixing

-9-

may be different during different stages in the formulation. These temperatures are not narrowly critical and will vary to provide faster mixing or better compatibility of ingredients according to observation of those skilled in the art. For example, pressure vessels may be utilized for the purpose of lowering ingredient melting and boiling points, where useful, in order to provide better dispersion of difficult-to-mix ingredients.

Mixing Procedure: While the formulations of the present invention may be manufactured continuously if desired, batch techniques will be more usually employed. Acrylic emulsions, water, corrosion inhibitors and neutralizing agents are mixed in a stainless vessel.

Quality Control:

The finished formulation, prior to packaging, will generally be checked for viscosity, solids content, freeze-thaw stability, film build, spray ability, corrosion-protection under accelerated conditions and other tests utilizing techniques well known to the coatings industry.

Application:

The formulations of the present invention may be applied to substrates to be protected by conventional application techniques, such as spraying, brushing, dipping, flow-coating, electrostatic airless spraying. Coating thickness can be varied by changing the formulation, the number of coats, or the amount applied per coat but in general will be in the range from about 0.5 to about 5 mils after drying.

-10-
EXAMPLES

Example 1

(Formulations according to the invention providing firm film for protection of underlying permanent paint layers and also providing easy removability with alkaline cleaners)

To a conventional unjacketed mixing kettle equipped with mild impeller rotary mixer or agitation are added, in order: 55.3 parts by weight of Neocryl BT-520, an alkali-soluble acrylic emulsion manufactured by Polyvinyl Chemical Industries and described above under "Acrylic Emulsions" at room temperature (about 20°C); 42.10 parts by weight of water (tap water) at tap temperature (approximately 15°C), these components are allowed to mix until homogenous, no substantial reaction is involved. To this mixture is added very slowly 1.79 parts by weight of aqua ammonia (28° Baume NH4OH) which will cause the mixture, previously milky, to become clear. This neutralizes the acid groups on the acrylic resin but involves no substantial exotherm. To this clear mixture is added 0.18 parts by weight of Triton X-100, a nonionic surfactant manufactured by GAF, 0.45 parts by weight of Cobratec-85, a sodium salt of a tolyltriazole manufactured by PMC Specialities, and 0.18 parts by weight of BYK-020, a defoamer manufactured by BYK Chemie. Agitation is continued during the addition of all of the ingredients. No heating is required. Agitation is continued for about two hours until the mixture is entirely homogenous.

The homogenous batch is sampled for quality control and the pH is found to be about 9 (a range of pH is preferably from about 8 to 10, more preferably from

-11-

about 8.5 to 9.5). Nonvolatiles are measured by wt% of evaporation and found to be approximately 23% (nonvolatiles will generally be in the range of from about 18 to 27, more preferably from about 20 to 25, and most preferably from about 21 to 24% though these can, of course, be reduced by dilution of the formulation, e.g. for specialized applications).

ASTM Method D-2369 is used to determine nonvolatiles.

Viscosity is found to be about 23 seconds using a Ford Number Four cup viscometer (preferred viscosity will be in the range of from about 15 to about 27, more preferably from 18 to about 25, and can also vary with dilution as needed).

Resulting product is tested for weathering resistance by applying it to a cold rolled 10 10 steel panel which has been painted with a Dupont acrylic enamel which is sprayed on. After drying for 24 hours, the test panel is subjected to a xenon light Weatherometer operated according to ASTM G-26-83 and resists over 300 hours of exposure to the Weatherometer without failure.

A panel which had been exposed for 300 hours to the Weatherometer was then sprayed with a cleaner composed of water, DPM (co-solvent) and Triton X-100 (surfactant) and 28° Be aqua ammonia. The temporary coating of the present invention is readily removed with gentle sponging (allow to set for 3-5 minutes). The alkaline cleaner effectively solubilizes the coating and it removes readily. Examination of the underlying acrylic enamel permanent finish shows no visible staining, no

-12-

apparent gloss reduction or other apparent softening or damage to the permanent film.

The coating composition exhibits good freeze/thaw stability over 5 cycles of 8 hours at 0°F followed by 16 hours at about 25°C and repeat.

Examples 2-13

(Formulations produced according to the techniques of Example 1, but using the respective parameters set forth in Table 2 provide the results described in Table 2)

Example VI is a commercial temporary protective formulation available from Eastman Kodak comprising:

(Eastman E43 Anionic Emulsion)

Eastman E43 Polyethylene	40 PBW
Tall Oil Fatty Acid	7 PBW
Morpholine	6 PBW
KOH	3 PBW
Sodium Metabisulfite	0.4 PBW
Isobutanol	4 PBW
Water	61 PBW

Example VII is a commercial temporary protective coating also available from Eastman comprising:

(Eastman E-10 Anionic Emulsion)

Eastman E10 Polyethylene	40 PBW
Tall Oil Fatty Acid	7 PBW
Morpholine	6 PBW
Water	103 PBW

MODIFICATIONS

-13-

Specific compositions, methods, or embodiments discussed are intended to be only illustrative of the invention disclosed by this specification. Variation on these compositions, methods, or embodiments are readily apparent to a person of skill in the art based upon the teachings of this specification and are therefore intended to be included as part of the inventions disclosed herein.

For example, pigments or non-staining dyes can be added to provide distinctive color and/or opacity, multiple coats can be used, compositions can be diluted as needed to provide desired film thickness and ease of application. These compositions will typically permit recoating with additional coats of similar compositions without wrinkling or lifting of the base coat. In fact, the second coating will generally cause some softening of the first layer of the temporary coating so that the two coats fuse together and form a desirably thick coat.

Reference to patents and other literature made in the specification is intended to result in such patents or literature being expressly incorporated herein by reference including any patents or other literature cited within such patents.

TABLE 2
(Parts by Weight)

Example Run #	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.	Comp.	Inv.	Comp.	Comp.	Comp.	Comp.	Comp.
Example Run #	B1641-84	B1641-79A	B1641-15	B1641-55B	B1641-76			B1595-168	B1595-149	B1595-142	B1595-100C	B1595-10III	B1595-188
Invention/Comp.	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.	Comp.	Inv.	Comp.	Comp.	Comp.	Comp.	Comp.
Acrylic Emulsion BY-520 (Diedrich XPD-1214 Kolon & Haas WS 24	55.3	32.2	37.6	32.2	32.2			50					100.0
Aniline 20% in Aqua Ammonia	1.79	1.2	1.3	1.2	1.2								
Corrosion Inhibitors (Cobratex 99 Cobratex TTUS	0.45	1.5		1.5	1.5								
Surfactants Triton X-100	0.18	0.2			2.0			2.5					
Diluents HYK 020 SWS 211	0.18	0.1		0.1	0.1								
Co-Solvents Isobutanol Water	42.10	1.5 63.7	23.5	3.5 61.5	1.5 61.5			47.5		70	05	50	
Other Additives Am. Hoechst Vp CTE Max Inra Chem WS 0215										30	15		
Comparative Formulations Allied Chemical Nontonic 110 Emulsion Eastman Antonic E-43 Emulsion Eastman Antonic E-10 Emulsion Durex 1546 Leveling Resin (1% Solution)			17.6			100.0	100.0		67			50	

TABLE 2 (con't)
(Parts by Weight)

Example Run #	EXAMPLE											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	B1641-84	B1641-84	B1641-15	B1641-55B	B1641-76			B1595-168	B1595-149	B1595-142	B1595-100C	B1595-188
Invention/Comp.	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.	Comp.	Inv.	Comp.	Comp.	Comp.	Comp.
Weatherometer	300hr	300hr	cracked	300hr ¹	300hr	cracked	cracked	300hr	300hr	300hr ⁵	300hr ⁵	300hr
Film Appearance	clear	clear	cracked	clear	clear	hazy	hazy	clear	opaque	clear	clear	transparent
Film Firmness	hard	hard	hard	hard	hard	hard	hard	hard	firm	soft	firm	hard
Removability with Alkaline Cleaner	excel.	excel.	fair	excel.	excel. ²	good ³	good ³	excel.	poor ⁴	-- ⁵	-- ⁵	poor, would not remove

RI-6115AUS

- 1 - Was unable to test for removability because film washed off during exposure.
 2 - Ran outdoors on 1986 Pontiac 6000 for 3 months exposure, excellent results up to 3 months.
 3 - Removed with cold water only, alkaline cleaner not required.
 4 - Material was water sensitive, cold water removable, stained paint film.
 5 - Stained painted substrate.
 6 - Film was washed off by weatherometer rock spray.

16

CLAIMS

1. Anti-corrosive, storage stable, water-based, water or co-solvent reducible, non-staining, dispersible coating compositions removable with water-based alkali cleaners at room temperature, capable of application and flow on solid substrates to form a firm but removable coating, said composition comprising:

- A. alkali soluble acrylic emulsion;
- B. water-soluble amine or aqueous ammonia;
- C. surfactant having a hydrolipo balance (HLB) of from about 10 to about 15; and
- D. water with optional co-solvents, corrosion inhibitors, UV additives, defoamers and other additives.

2. A composition according to Claim 1 wherein the surfactant comprises a alkyl phenoxy polyethoxy ethanol or other nonionic surfactant.

3. A composition according to Claim 1 comprising 0 to 30% weight co-solvents selected from the group consisting of alcohols and glycol ethers.

4. A composition according to Claim 1 further including about 0.1 to 15% by weight of corrosion inhibitors.

5. A composition according to Claim 4 in which co-solvents comprise faster evaporating alcohols

17

selected from the group consisting of methanol, ethanol, isobutanol, secondary butanol.

6. A composition according to Claim 5 comprising corrosion inhibitors selected from the group consisting of benzotriazoles, tolytriazoles, ammonium salts of dichromates and molybdates.

7. A composition according to Claim 1 in which the acrylic emulsion is an acrylic copolymer emulsion having acid value in the range of about 20-200.

8. A composition according to Claim 7 comprising the sodium salt of tolytriazoles.

9. A method for coating solid substrates wherein a composition according to Claim 1 is applied to a painted substrate by dipping, brushing, rolling and/or spraying.

10. An article of manufacture comprising a painted substrate coated with a film derived from a composition of Claim 1.

AMENDED CLAIMS

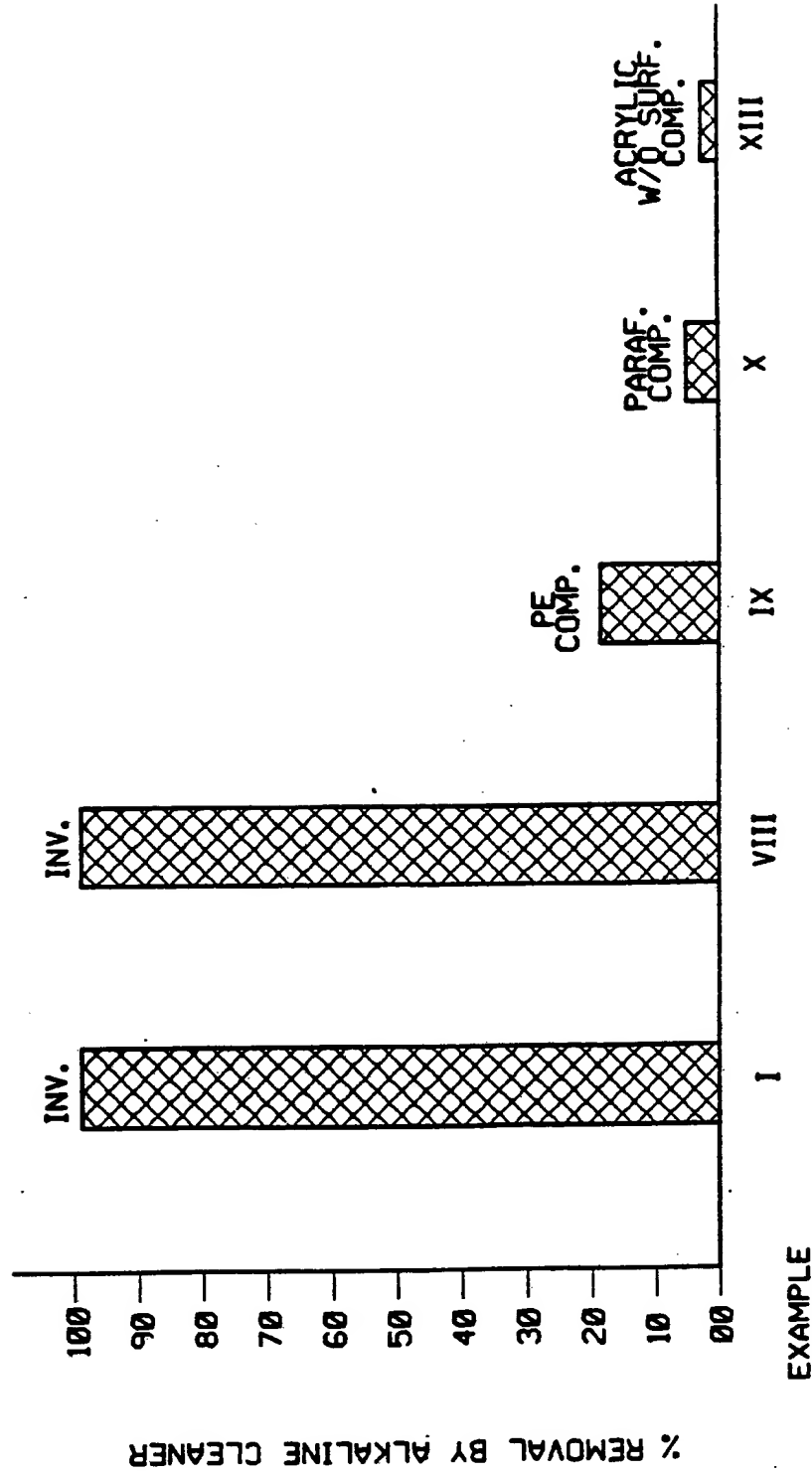
[received by the International Bureau on 28 November 1989 (28.11.89)
original claim 1 amended; remaining claims unchanged (1 page)]

1. Anti-corrosive, storage stable, water-based, water or co-solvent reducible, non-staining, dispersible coating compositions removable with water-based alkali cleaners at room temperature, capable of application and flow on solid substrates to form a firm but removable coating, said composition comprising:

- A. alkali soluble acrylic emulsion;
- B. 0.1 to 20 parts by weight of said composition of a water-soluble amine or aqueous ammonia;
- C. 0.1 to 10 parts by weight of a surfactant having a hydrolipo balance (HLB) of from about 10 to about 15; and
- D. Water with optional co-solvents, corrosion inhibitors, UV additives, defoamers and other additives.

- 1/2 -

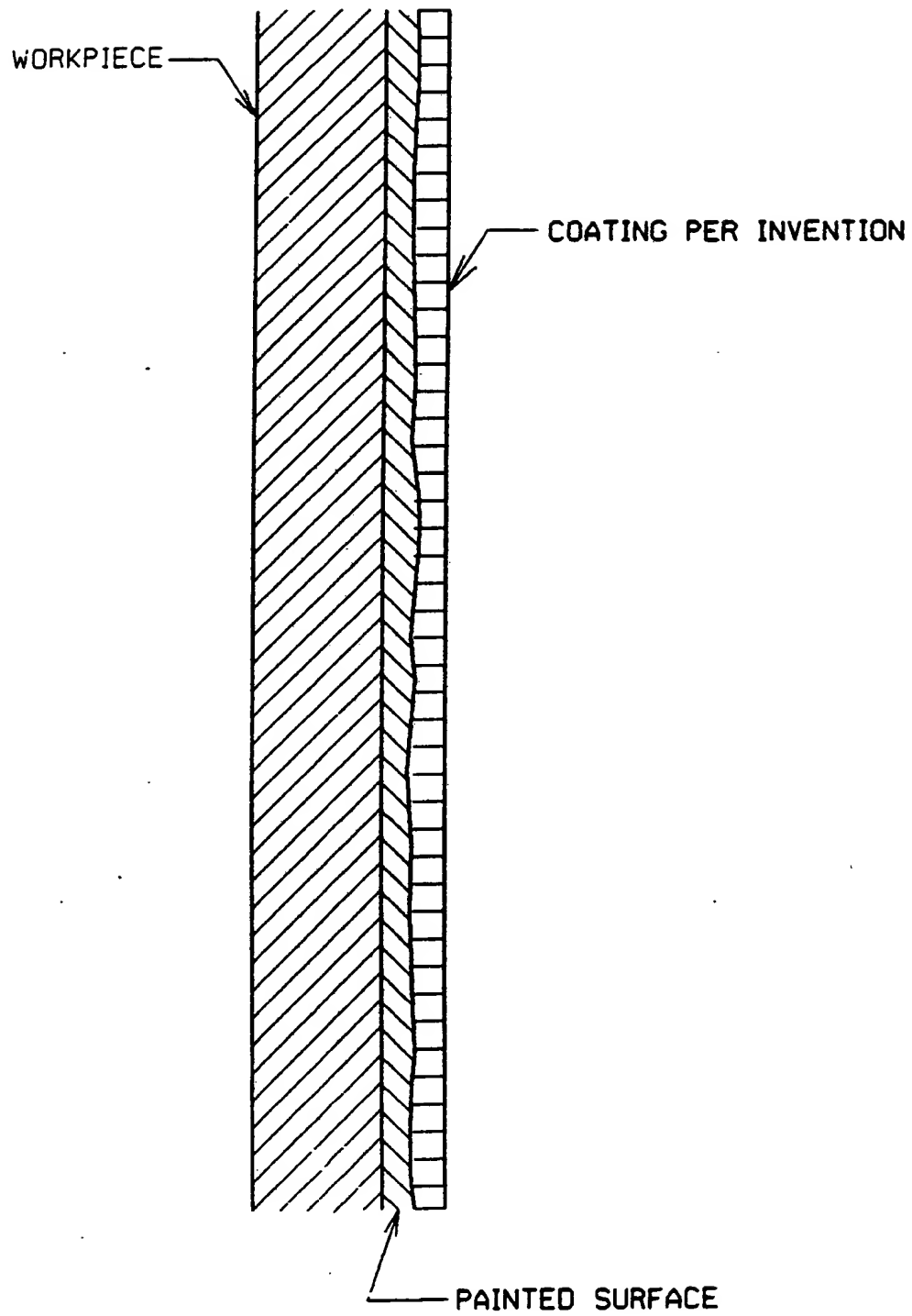
FIG.1



C₁ -65 WEATHEROMETER
EXPOSURE FOR 300 HOURS
ASTM G-26-83

- 2 / 2 -

FIG.2



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/01980

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 09 D 5/00																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC ⁵</td> <td style="padding: 5px;">C 09 D</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	C 09 D											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 60%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 4626559 (W.H. SADLER) 2 December 1986, see claims 1,5,9 --</td> <td style="text-align: center; vertical-align: top;">1,4</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>EP, A, 0162611 (I.C.I.) 27 November 1985, see claims 1-3,5,6,9; page 7, lines 17-22; page 15; page 8; page 9, lines 23-29; page 4, lines 7-14</td> <td style="text-align: center; vertical-align: top;">1,2</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>--</td> <td style="text-align: center; vertical-align: top;">3,5,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4070510 (J.E. KAHN) 24 January 1978, see column 12, example 8; formulations A,B,D (footnotes) ----</td> <td style="text-align: center; vertical-align: top;">1,2</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4626559 (W.H. SADLER) 2 December 1986, see claims 1,5,9 --	1,4	Y	EP, A, 0162611 (I.C.I.) 27 November 1985, see claims 1-3,5,6,9; page 7, lines 17-22; page 15; page 8; page 9, lines 23-29; page 4, lines 7-14	1,2	A	--	3,5,7	Y	US, A, 4070510 (J.E. KAHN) 24 January 1978, see column 12, example 8; formulations A,B,D (footnotes) ----	1,2
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A	--	3,5,7															
Y	US, A, 4070510 (J.E. KAHN) 24 January 1978, see column 12, example 8; formulations A,B,D (footnotes) ----	1,2															
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁴ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center; padding: 5px;">24th August 1989</td> <td style="text-align: center; padding: 5px;">28 SEP 1989</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center; padding: 5px;"> T.K. WILLIS </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	24th August 1989	28 SEP 1989	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	T.K. WILLIS							
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EUROPEAN PATENT OFFICE	T.K. WILLIS																

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8901980
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 18/09/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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